3 Hypotheses of Causes of the Ozone Weekend Effect

This chapter presents various hypotheses that have been advanced as possible explanations of the ozone weekend effect. These hypotheses are not necessarily complete solutions; each might account for all, for part, or for none of the observed differences in measured ozone on weekdays versus weekends.

Explaining the weekend effect is not a simple task because ozone formation, transport, and destruction in the lower atmosphere is a highly complex process. It is not surprising, therefore, that multiple hypotheses have been proposed concerning the cause(s) of the ozone weekend effect. Seven hypotheses are considered here. The hypotheses address temporal, spatial, and compositional changes in emissions from weekdays to weekends and how these changes might interact with meteorological and photochemical processes to produce the observed weekday to weekend differences in ozone concentrations. The seven hypotheses are:

1. **NO_X reduction**: more ozone is formed on weekends because urban areas of California are "VOC-limited" and proportionately lower NO_X emissions on weekends increase the VOC/NO_X ratio; nonlinear ozone photochemistry then generates more ozone on weekends than on weekdays.

2. **NO_X timing**: more ozone is formed on weekends because a significant portion of NO_X emissions is shifted to later in the day (and also toward the suburbs). This shift in the timing of NO_X emissions causes O_3 to form more efficiently on weekends than on weekdays.

3. **Carryover at ground level**: more ozone is formed on weekends because extra O_3 precursors are emitted on Friday and Saturday evenings. Carryover of more precursors then generates more O_3 on weekends than weekdays.

4. **Carryover aloft**: more ozone is measured on weekends because the amount of O_3 carryover aloft depends on a variety of factors, including precursor emissions on the previous day; with lower precursor emissions on weekends than weekdays, the O_3 aloft contributes proportionately more to surface O_3 levels on weekends than on weekdays.

5. **Increased weekend emissions**: more ozone is formed on weekends because recreational, home, and lawn and garden activities produce more ozone precursors on weekends and these produce more ozone on weekends than on weekdays.

6. **Aerosols and UV radiation**: more ozone forms on weekends because aerosol emissions in the early morning and mid-day are lower on weekends, allowing more solar radiation to reach lower into the atmosphere and to generate more ozone on weekends than on weekdays.

7. **Surface O_3 quenching:** less ozone is destroyed (quenched) near the ground on weekends because ozone-quenching emissions of NO at ground level are lower throughout the day on weekends; therefore, monitors at the surface measure more ozone on weekends than on weekdays.

The ARB staff has reviewed the available data to assess which hypotheses are consistent with the data and are, therefore, plausible. Unfortunately, neither the empirical data nor the modeling data are sufficient at this time to demonstrate which hypotheses govern or contribute to the ozone weekend effect. Limitations concerning these data are discussed below. Specific, point by point comparisons between theory and observations are given in this chapter. General conclusions regarding the seven hypotheses are included in Chapter 5.

Limitations of the empirical data

Though the available data indicate that several hypotheses are plausible causes of the ozone WE effect, the data are not sufficient to quantify the contributions of these processes. Strategic studies of air quality, meteorology, and emissions are needed to resolve the outstanding questions. In addition, computer models must achieve or demonstrate satisfactory performance in areas that have rarely received significant attention. Additional study is needed despite the fact that California's routine and specialized databases for air quality, emissions, and meteorology are among the most extensive in the world. The routine data clearly reveal the existence and the magnitude of the ozone weekend effect, but these data do not tell us why it happens. The routine air-monitoring network was designed to address air quality status and trends in a general fashion. To meet these goals, it was sufficient to gather data regarding air quality at the surface.

Surface data provide a wealth of information about a small fraction of the ozone-forming system. Surface data usually do not represent conditions in the air aloft, from 100 to 1000 meters above the ground, where the vast majority of the ozone we breathe is formed. Understanding the conditions aloft is a central issue for hypotheses 1, 4, and 7 and may also be important for hypotheses 2 and 6.

Air quality and meteorology data that directly represent conditions aloft are scarce for two reasons. First, such data are often difficult and expensive to collect. Second, their potential importance has not always been appreciated; after all, people do not live hundreds of meters above the ground.

Limitations of the modeling data

Computer models that simulate photochemical air pollution are promoted by some as the answer to questions concerning the cause(s) of the ozone WE effect. These models play an important role in evaluating the likely effects of emission reductions included in State Implementation Plans. The ozone WE effect, however, presents a more difficult problem, and the available models have significant omissions and uncertainties that limit their ability to isolate and quantify the effects of several hypotheses, including hypotheses 1, 2, 4, 5, and 7.

An appraisal of model performance is a standard element of a photochemical simulation study. However, these performance appraisals have rarely focused on some issues vital to the ozone WE effect. In point of fact, such appraisals may not be possible since empirical data to which simulated pollutant levels can be compared are rarely available at the times and places that are critical for modeling the ozone weekend effect. These and other limitations in the available models preclude confident conclusions based on simulations of the ozone weekend effect. On a positive note, substantial progress has been made in recent years in preparing day-of-week emission inventories and in developing episodes for modeling that include both weekdays and weekends.

Limited applicability to plans for attaining ozone standards

The policy implications of the ozone weekend effect may depend on quantitative assessments that are especially difficult in some key circumstances. For example, on days with high ozone concentrations, the ozone weekend effect currently appears to be about 20% in the coastal metropolitan areas and 5% in the interior valleys. In addition, the difference between weekdays and weekends appears to decrease substantially, perhaps by half, when meteorological conditions strongly favor ozone formation. Under such conditions in the South Coast Air Basin, one may need to allocate a weekend effect of 15% among multiple contributing processes. It can be very difficult to isolate an effect of 10% or less attributable to each participating process.

There are a number of reasons why staff does not believe the ozone weekend effect is representative of the ozone impacts associated with an emissions control program (see Conclusion #8 in Chapter 5). Until the cause(s) of the ozone weekend effect are satisfactorily identified and quantified, it has limited applicability to plans for attaining ozone standards. At this time, some of the plausible hypotheses contradict each other concerning the efficacy of NO_X reductions as an ozone abatement strategy. For example, both the "NO_X-reduction" hypothesis and the "surface ozone quenching" hypothesis attribute the weekend effect to reduced NO_X emissions on weekends. However, these hypotheses identify different mechanisms through which the reduced NO_X emissions affect daily maximum ozone levels. As formulated, the two hypotheses have opposite implications concerning the efficacy of regulatory reductions of NO_X emissions.

It is likely that multiple hypotheses contribute to the ozone weekend effect to a greater or lesser degree. We examine each hypothesis separately rather than jointly because their distinct mechanisms may have different implications with respect to regulatory emission reductions.

Expanded discussions and evaluations of hypotheses

In this section, we address the seven hypotheses in some detail. For each hypothesis, we first present a brief synopsis. Second, we describe the underlying theory that caused each hypothesis to be suggested initially. Third, we compare hypothetical expectations to related observations. We conclude the discussion of each hypothesis by addressing some of the limitations of the available data.

Hypothesis #1: NO_X-reduction

- **Synopsis**

The NO_X-reduction hypothesis asserts that more ozone is formed on weekends than on weekdays. The additional ozone formation is attributed to reduced emissions of NO_X on weekends compared to weekdays. The mechanism that produces higher ozone on weekends is a complex mechanism that produces more ozone when NO_X emissions are reduced in a "VOC-limited" system. That is, non-linear photochemistry causes O_3 to increase on weekends compared to weekdays as NO_X decreases more than VOC.

Nonlinear photochemistry has been studied for many years. When ozone formation is limited by the availability of VOC, conditions are described as "VOC-limited" or "VOC sensitive". Air quality models based on laboratory results indicate that <u>reducing</u> NO_x under VOC-limited conditions may lead to <u>higher</u> ozone concentrations (see Figure 3-1). A key cause of this counter intuitive effect is the hydroxyl radical, an essential part of ozone-forming reactions. Hydroxyl radicals react with VOC to help promote ozone formation. When VOC are less available, however, more hydroxyl radicals can react with NO_2 to form nitric acid, which until recently was thought to remove NO_X irreversibly from the ozone formation process.

The NO_X-reduction hypothesis further asserts that ozone formation in most areas of the South Coast Air Basin are VOC-limited and that NO_X emissions decrease on weekends relatively more than VOC emissions decrease. A consequence of proportionally more NO_x reductions on weekends is that the ratio of VOC to NO_x in the ambient air tends to be greater on weekends compared to weekdays. The higher VOC to NO_x ratio would then lead to greater ozone formation on weekends than on weekdays in the SoCAB. However, the magnitude of the ozone disbenefit depends on the specific situation (Milford et al., 1989).

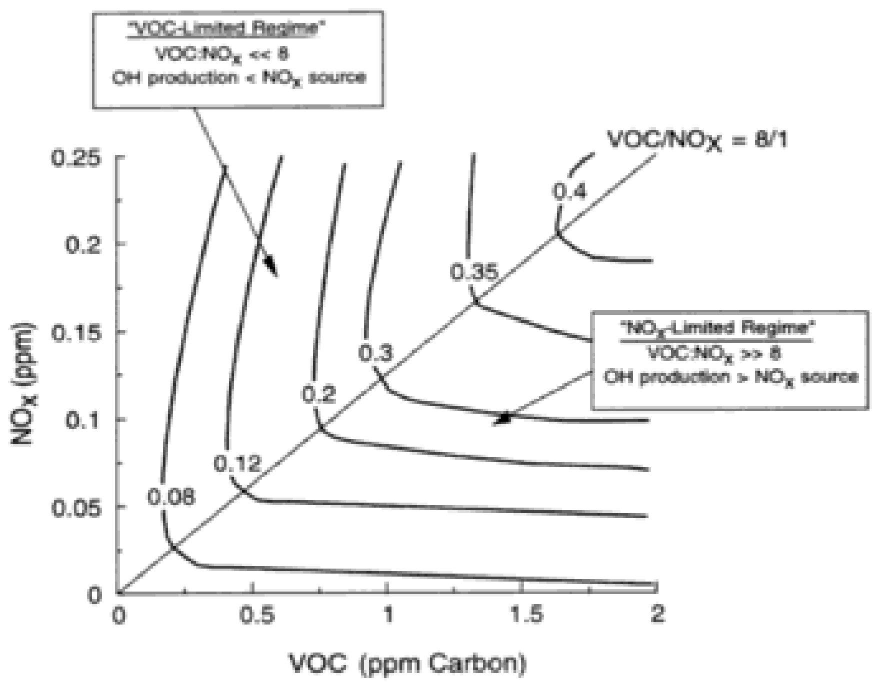
- **Theory**

A brief review of the photochemistry involved in ozone formation is given in the preceding chapter. As noted there, the ratio of VOC to NO_X is an important factor that helps determine the maximum ozone generated from initial concentrations of these ozone precursors. When VOC is plentiful relative to NO_X, ozone formation is limited by the amount of NO_X available. Such situations are called "NO_X-limited" or

"NO_X sensitive." Under NO_X-limited conditions, we expect NO_X reductions to reduce the peak ozone, while VOC reductions have little effect on peak ozone.

When NO_X is plentiful relative to VOC, ozone formation is limited by the amount of VOC available. These situations are called "VOC-limited" or "VOC sensitive." Under VOC-limited conditions, we expect VOC reductions to reduce the peak ozone, but NO_X reductions may cause the peak ozone to increase. These properties are represented in the Empirical Kinetics Modeling Approach (EKMA). A simple "EKMA" diagram is shown in Figure 3-1. In the figure, the VOC to NO_X ratio that produces the maximum ozone concentration is about 8 ppmC/ppm. In any particular case, the ratio that produces the highest ozone depends on the specific mixture of VOC species, because VOC species may differ in their potential to promote ozone formation. Furthermore, the maximum ozone depends on a number of additional factors, including meteorology and atmospheric transport. Despite the limitations and biases associated with accurately measuring VOC/NO_X ratios, the ratio does provide a useful framework for describing the complexities of ozone formation.

Figure 3-1. Schematic EKMA diagram illustrating the relationship between concentrations of VOC and NO_X and the resulting maximum ozone concentration (parts per million).



Source: National Research Council (1999) *Ozone-Forming Potential of Reformulated Gasoline,* National Academy Press, Washington, DC.

The NO_X-reduction hypothesis asserts that present-day emissions patterns in the South Coast Air Basin cause conditions throughout the basin to be in the VOC-limited category on weekdays; that is, the VOC/NO_X ratios are generally less than 8 ppmC/ppm. On weekends, the hypothesis assumes that NO_X is reduced substantially more than are VOCs. Consequently, the weekend VOC/NO_X ratio is higher than the VOC/NO_X ratio on weekdays and this causes slightly higher ozone concentrations on weekends as implied by the EKMA diagram in Figure 3-1.

- **Hypothetical expectations and related observations**

If the NO_X reduction hypothesis contributes substantially to the weekend effect, the expectations below are reasonable. With each expectation, related observations are given to help evaluate the plausibility of the hypothesis.

Expectation: Typical VOC/NO_X ratios on weekdays and weekends should be less than 8 ppmC/ppm, indicating "VOC-limited" conditions (see the EKMA diagram in Figure 3-1).

Observation: In recent years in the South Coast Air Basin, most measured VOC/NO_X ratios are less than eight. In addition, various measures of sensitivity to VOCs and NO_X also indicate that the prevailing ozone formation regime is VOC-limited.

Expectation: Ambient levels of NO_X will decrease on weekends more than do ambient levels of VOCs. As a result, the VOC/NO_X ratio on weekends should be higher than on weekdays for corresponding hours of the day.

Observation: Measurements of ambient VOCs and NO_X in the SoCAB indicate that weekend NO_X emissions during daylight hours are about 40% lower than weekday NOx emissions, while the corresponding VOC emissions are about 25% lower than weekday VOC emissions. This observation is a reasonably reliable indicator of changes in the rates of surface-based emissions. Average VOC/NO_X ratios on weekends are approximately 10 to 20 percent higher on Saturday and 20 to 30 percent higher on Sunday compared to weekdays.

Expectation: Ozone concentrations should increase earlier on weekends than on weekdays because radicals are more likely to participate in reactions that form ozone and less likely to participate in reactions that retard ozone formation.

Observation: In areas where the ozone WE effect occurs, ozone levels do increase earlier on weekends than on weekdays.

Expectation: The NO_2 to NO ratio should be higher on weekends than on weekdays because the photochemical system is more active and produces more ozone and more radicals that convert NO to NO_2 more rapidly.

Observation: The NO_2 to NO ratio does tend to be higher on weekends than on weekdays at all monitoring locations in Los Angeles and Orange Counties for which data were analyzed.

Expectation: If VOC/NO_x ratios move further into the "VOC-limited" range, the magnitude of the ozone WE effect should increase.

Observation: Over the last twenty years, VOC/NO_x ratios have decreased and moved further into the "VOC-limited" range. During this period, the magnitude of the ozone WE effect has increased.

- **Limitations**

The primary limitation of all the observations discussed above is their reliance, almost exclusively, on surface-based measurements. These data represent the conditions near the ground, which may differ greatly from the conditions above the ground where most of the ozone we breathe is formed. At this time, empirical data on conditions above ground level are relatively scarce. Nevertheless, the available data indicate large differences between the conditions at the surface and the conditions aloft through most of the day.

Two limitations relating to VOC data are important. First, VOC data are available from a relatively small number of monitors, and the measurements are confounded by meteorological variations. Our ability to characterize VOC/NO_X ratios with high accuracy throughout the day is limited. As a result, measured VOC/NO_X ratios on weekdays and weekends vary greatly and their ranges overlap substantially.

Second, many VOC measurements do not fully account for the reaction products formed from the VOC emissions. In the air, chemical reactions cause the VOC emissions to be converted to compounds that contain oxygen. Many of these oxygenated compounds are not included in routine laboratory analyses. Standard VOC measurements are about 40% below true values while NO_X measurements are overestimated by some variable percent. As a result, the actual conditions may be less "VOC-limited" than the data indicate.

Hypothesis #2: NO_X-timing

- **Synopsis**

The NO_X-timing hypothesis presumes that the timing of emissions on weekends contributes significantly to the ozone WE effect. In particular, the NO_X-timing hypothesis asserts that much of the NO_X emissions is delayed on weekends until the photochemical system is highly active and ambient NOx concentrations are low. Under these conditions, the delayed NO_X emissions are able to produce ozone more efficiently compared to the NO_X emitted on weekdays.

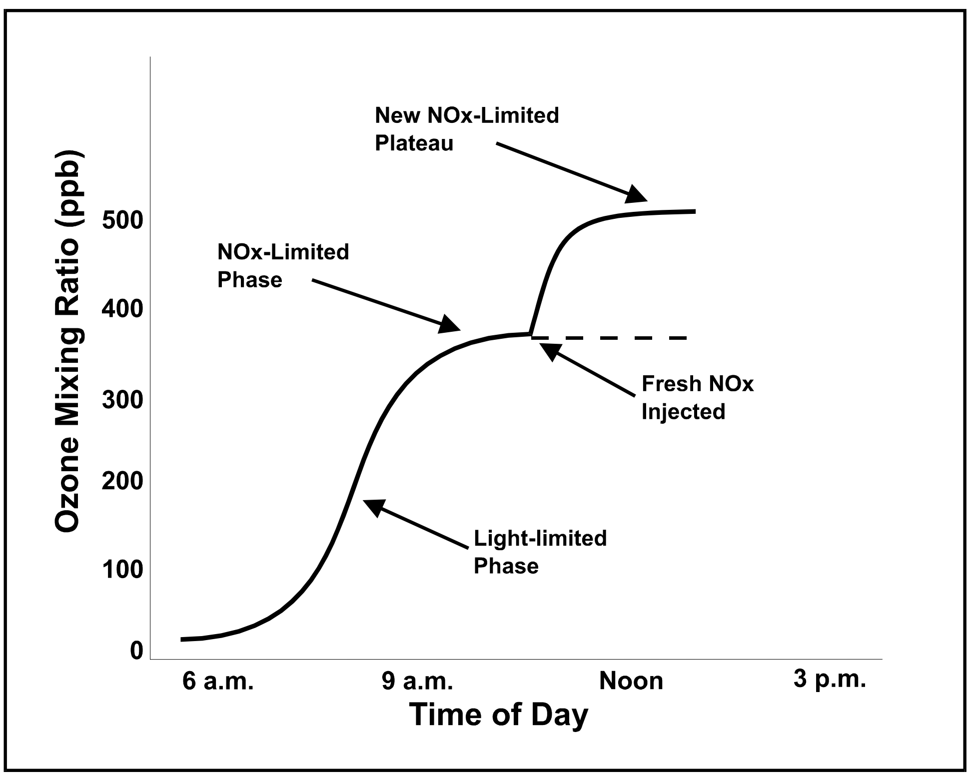
- **Theory**

In laboratory experiments, NO_X can strongly promote ozone formation when added to an active photochemical system that has become NO_X-limited. In such a case, the NO_X appears to be more efficient at producing ozone compared to NO_X emissions that enter a less active, less mature system. Figure 3-2 illustrates this phenomenon.

The NO_X-timing hypothesis asserts that the temporal distribution of NO_X emissions on weekends differs from that on weekdays. In particular, NO_X emissions are delayed on weekends so that they occur later in the day compared to weekdays. Because the NO_X emissions occur later in the day, they enter a more active photochemical system, participate in ozone-generating reactions more efficiently, and lead to higher ozone on weekends than on weekdays.

According to Figure 3-2, NO_X and VOCs are present as the sun begins to rise. As sunlight increases, photochemical reactions increase and the system may move through an initial “light-limited” (also known as “radical-limited“ or “VOC-limited”) phase onto a “NO_X-limited" plateau. When a fresh dose of NO_X is then injected, ozone production does not decrease but increases to a higher NO_X-limited plateau. Even VOC-limited systems tend to move toward NO_X-limited plateaus as the day progresses (Lu and Chang, 1998). This happens because VOCs persist in the atmosphere longer than NO_X. The NO_X is removed relatively quickly from the photochemical system and eventually becomes a limiting factor in ozone formation.

Figure 3-2. Illustration of NO_X timing effect in the laboratory.

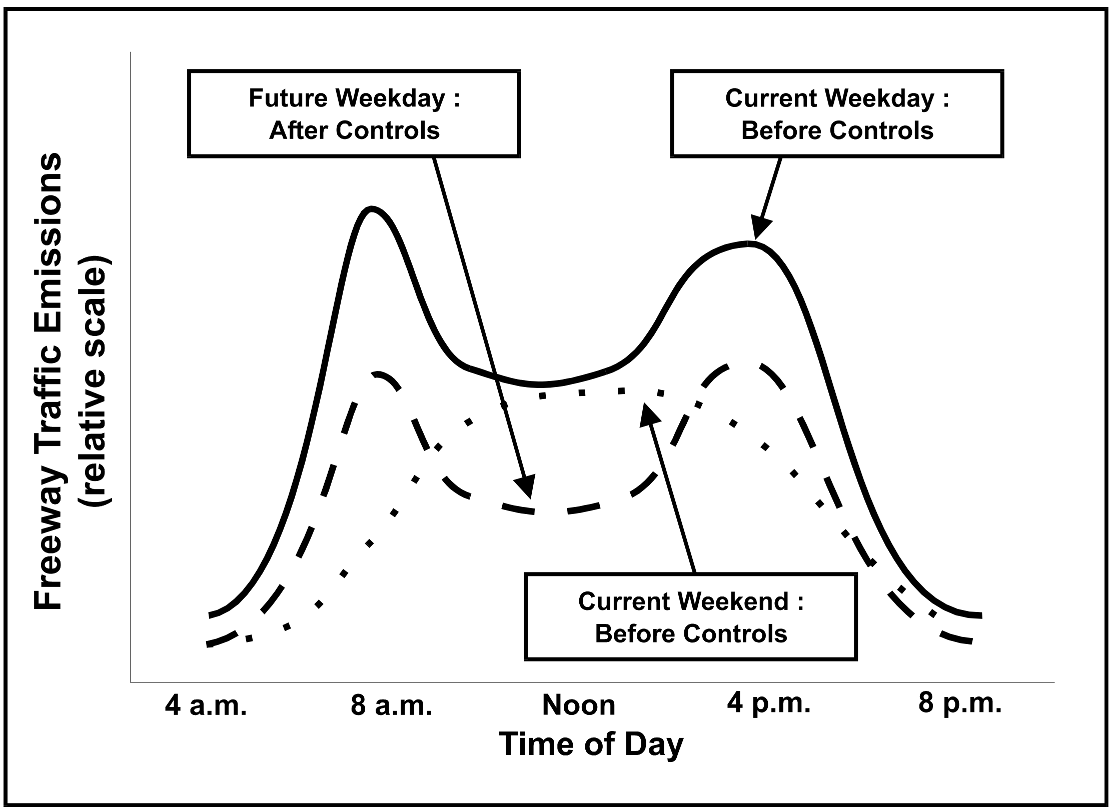


Source: Adapted from Figure 4 in Hess, et al., 1992. Mixing ratios were large because this was a smog chamber experiment. Also, the VOC/NOx ratio at the start of the test was quite large.

A central difference between the NO_X-timing hypothesis and the NO_X-reduction hypothesis can be illustrated using Figure 3-3. The figure shows hypothetical hourly emissions from freeway traffic on current weekdays (solid line), current Sundays (dotted line), and future weekdays after implementing NO_X control measures (dashed line). In Figure 3-3, the total NO_X currently emitted on Sundays is similar that emitted on a future weekday. Of course, the timing of the emissions is dramatically different.

The NO_X-reduction hypothesis (#1) asserts that the ozone produced by hourly NO_X emissions that follow the dashed profile is the same as the ozone that would be produced if the same total amount of NO_X followed the dotted profile instead. The NO_X-timing hypothesis (#2), on the other hand, asserts that the dotted profile would lead to more ozone than would the dashed-line profile. The difference is important because the two hypotheses may have different policy implications concerning NO_X reductions for ozone abatement.

Figure 3-3. Comparison of hypothetical hourly emission profiles from freeway traffic (light and heavy duty) before and after emission control, based on activity patterns for traffic at Weigh-in-Motion stations.



- **Hypothetical expectations and related observations**

If the NO_X-timing hypothesis contributes substantially to the weekend effect, the expectations below are reasonable. With each expectation, related observations are given to help evaluate the plausibility of the hypothesis.

Expectation: The timing of emissions on weekends should be significantly different than the timing of emissions on weekdays. In particular, NO_X emissions should be relatively low in the morning compared to the emissions at mid-day.

Observation: In the SoCAB, on-road motor vehicles account for more than 60% of basinwide NO_X emissions. When all mobile sources are considered, they account for almost 90% of NO_x emissions in the SoCAB. Activity patterns for on-road motor vehicles indicate substantial differences in the timing of activity between weekdays and weekends (Figure 3-4 and Figure 3-5 are the basis for Figure 3-3 above). In addition, weekend emissions from freeway activity are highest around mid-day on weekends.

Expectation: Most of the atmosphere where anthropogenic ozone is formed, from ground level to 1500 meters aloft, should be in a NO_X-limited condition at some point leading up to the time when the daily maximum ozone is measured on weekend days.

Observation: The surface data do not indicate that the system reaches NO_X-limited conditions. Data that reveal the conditions aloft are extremely scarce. The limited observations available indicate that conditions aloft are often very different from the simultaneous conditions at ground level. In particular, NO_X concentrations aloft are almost always much lower than at the surface, and almost all of the NO_X is in the form of NO_2. It is possible that a large portion of the ozone-forming system is NO_X-limited even though the surface data suggest otherwise.

- **Limitations**

The primary limitation of the observations discussed above is the lack of data on the photochemical conditions in the air aloft (100 to 1500 m above the ground). Although there is good reason to think that conditions aloft are frequently NO_X-limited, sufficient empirical data to directly confirm are not available.

The significance of the NO_X-timing hypothesis is not easily assessed using the photochemical simulation models available today. Reliable data on conditions aloft and real-world emissions on weekends are important to acquire so model performance can be evaluated appropriately. In addition, the photochemistry associated with relatively low levels of NO_X near ground level and even lower levels aloft needs to be better characterized in modeling mechanisms.

Figure 3-4. Freeway activity of light-duty vehicles by day-of-week – composite of Y2000 data for 11 Weigh-in-Motion stations in California's South Coast Air Basin.

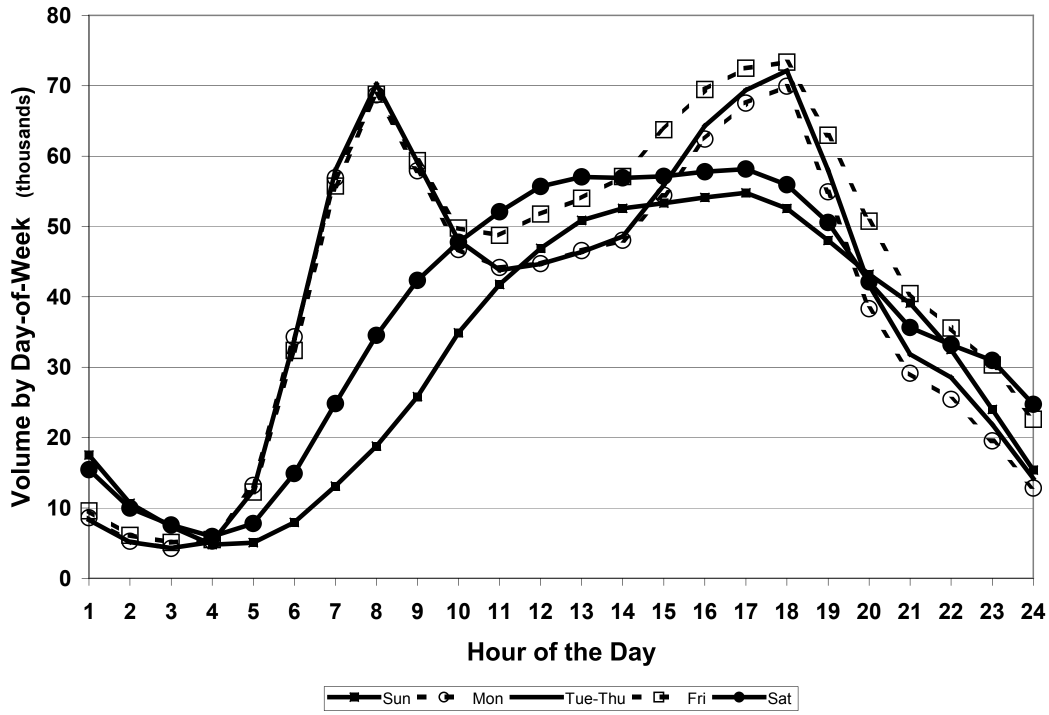
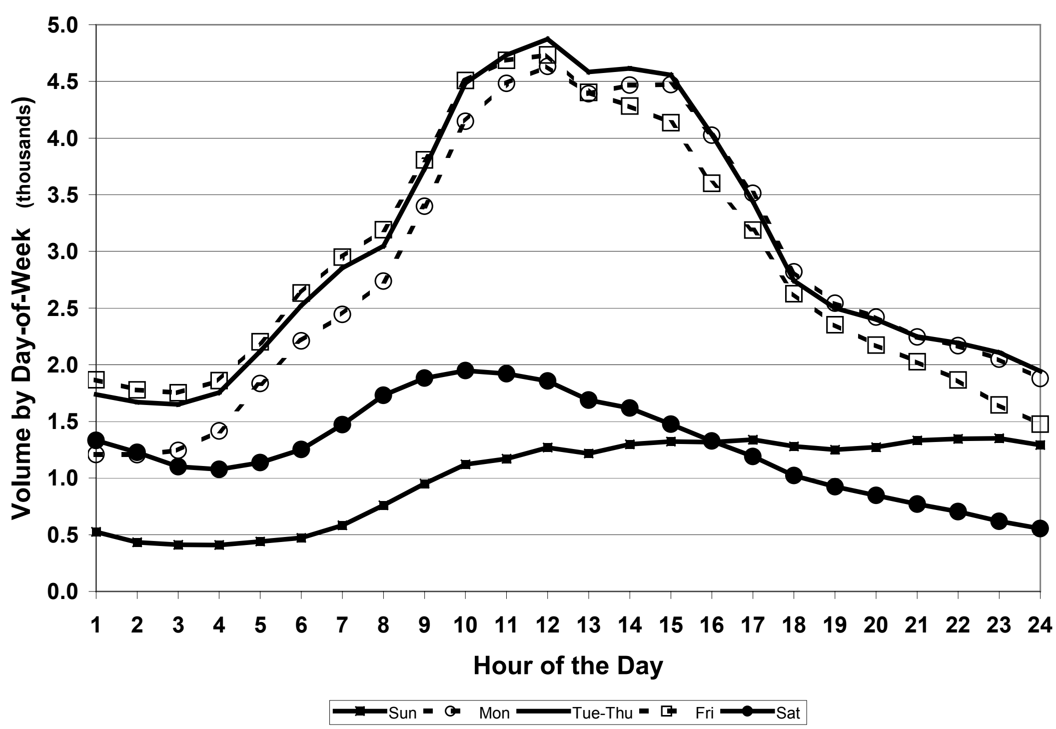


Figure 3-5. Freeway activity of heavy-duty vehicles by day-of-week – composite of Y2000 data from 11 Weigh-in-Motion stations in California's South Coast Air Basin.



Hypothesis #3: Carryover near ground-level

- **Synopsis**

The hypothesis concerning carryover near ground level does not involve complex theory. It simply asserts that the higher weekend ozone concentrations occur because extra emissions from increased traffic activity on Friday and Saturday nights participate in ozone formation during the daylight hours that follow. Carryover near the ground occurs because a layer of cool air forms at ground level as radiant cooling takes place and remains there overnight.

According to this hypothesis, traffic is higher on Friday and Saturday nights compared to other nights. Increased traffic would cause additional emissions of VOCs and NO_X to be injected into the nocturnal boundary layer. These extra emissions of ozone precursors then carry over and lead to greater ozone formation after sunrise on the following day.

- **Theory**

Influence of meteorology on emissions at the surface

Sometime after mid-day and before sunset, the radiant energy going out from the Earth's surface exceeds the incoming radiant energy. At that point, the surface and the air near the surface begin to cool. Vertical mixing of the air due to convection ceases when the potential temperature (as if the air were at sea-level pressure) of the air near the ground is lower than the potential temperature of the air above it.

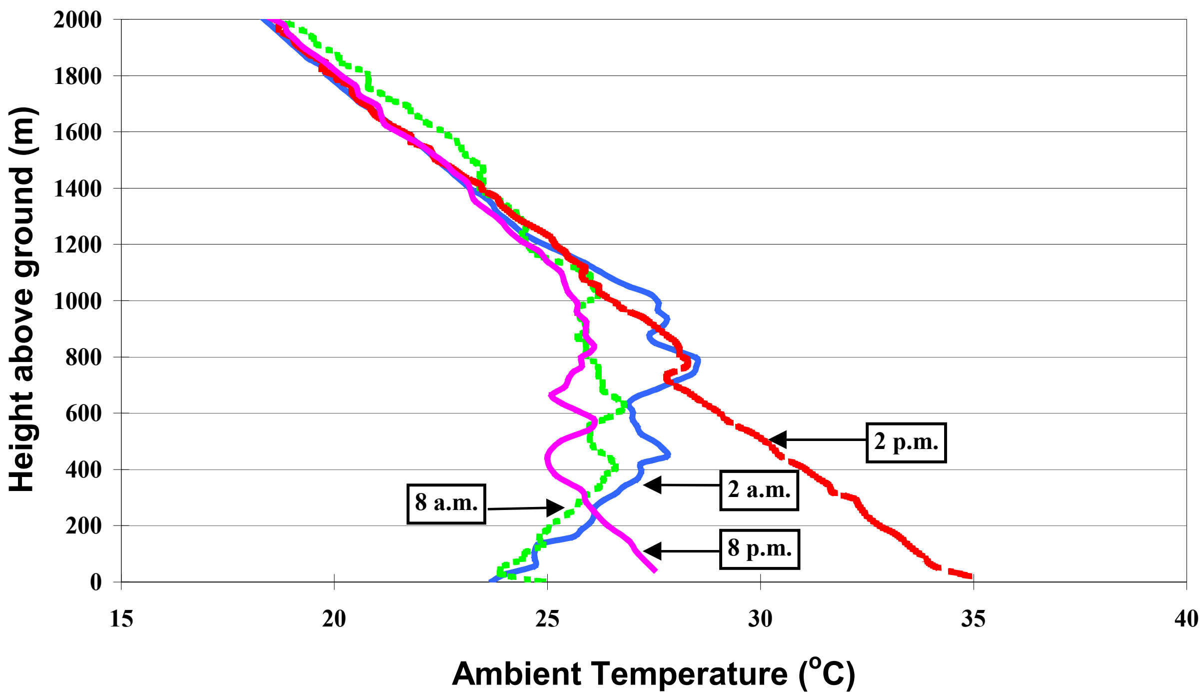
The cooling process continues overnight as infrared radiation dissipates heat from the surface. A nocturnal boundary layer (NBL) is the result. This layer of air is stable and remains near the surface. Although some turbulent mixing may continue to take place at night, such mixing is commonly limited to a relatively shallow layer.

This phenomenon happens because warm air rises and cool air sinks. When air is warmer than the air above it, the air will rise (cooling as it does so) until it encounters air that is equally warm, and there it stops. As the sun sets, the air near the ground tends to cool fastest, so it stays close to the ground. Figure 3-6 illustrates patterns of air temperature from the surface through 2000 meters at Riverside, California at different times of the day.

- **Hypothetical expectations and related observations**

If the carryover near ground-level hypothesis contributes substantially to the weekend effect, the expectations below are reasonable. With each expectation, related observations are given to help evaluate the plausibility of the hypothesis.

Figure 3-6. Examples of vertical temperature profiles at 2 a.m., 8 a.m., 2 p.m., and 8 p.m. on August 23, 1997 at Riverside, California.



Expectation: Major sources of VOC and NOx should be greater on Friday and Saturday nights compared to other nights. In particular, the largest source of ozone precursors, traffic, should be greater on Friday and Saturday nights than on other nights.

Observation: The day-of-week traffic patterns shown above in Figure 3-4 indicate that an extra measure of light-duty vehicle activity occurs on Friday night (into Saturday morning) and Saturday night (into Sunday morning). Figure 3-5, however, indicates that heavy-duty truck traffic is particularly low during these periods. Depending on the mix of vehicles, the composition of the emissions injected into the NBL on Friday and Saturday nights may be different from the usual composition. If light duty vehicles increase relative to heavy-duty diesel vehicles, the emissions that carryover to the following day may be richer in VOCs and less rich in NO_X. The currently available data are not sufficient to resolve such considerations at this time.

Expectation: Pollutant levels in the ambient air should be significantly greater at sunrise on Saturday and Sunday relative to the other days of the week.

Observation: Though some data imply that average levels of VOCs and NO_X at sunrise on Saturday and Sunday are greater than the levels on other days, the modest increase does not appear to be a major contributor to the ozone weekend effect.

- **Limitations**

Although traffic activity on freeways can be assessed with encouraging accuracy, measurements of traffic activity on surface streets are scarce. Some data indicate that the surface street patterns are roughly parallel to the freeway patterns, but a full assessment of surface street traffic by day of week is not yet available.

Hourly measurements of VOCs have been limited to a small number of locations using instruments that do not capture the full range of VOC species. In fact, hourly data are no longer collected in the SoCAB and the VOC samples that are collected continue to be incomplete. Aggregate samples collected across 3 and 24 hours provide information on a wider range of VOC species but lack the resolution in time needed to see whether early morning VOC levels on Saturday and Sunday are substantially higher compared to other days. With more complete and timely VOC data, carryover near the ground might prove to contribute significantly to the ozone weekend effect.

Hypothesis #4: Carryover Aloft

- **Synopsis**

According to the carryover aloft hypothesis, a reservoir of pollutants often carries over from one day to the next above the nocturnal boundary layer. This reservoir can be large and rich in ozone, VOCs and possibly radical precursors during the night (e.g., O_3, HCOH, HONO, and PAN). These pollutants represent a legacy from the emissions and meteorological conditions that prevailed "yesterday." Pollutants from one day that carry over in an overnight reservoir aloft often mix down to the surface the next day (today), and affect ground-level ozone measurements.

The carryover aloft hypothesis asserts that pollutants generally carryover aloft on all days of the week. In addition, it presumes that the carryover of pollutants is proportional to the previous day's emissions but that the O_3 formation regime can differ. Because emissions presumably decrease on Saturdays and again on Sundays, carryover aloft is expected to exert greater influence on weekend surface ozone than on weekday ozone.

- **Theory**

Meteorology and carryover of pollutants aloft

When the nocturnal boundary layer (NBL) develops at the surface overnight (see the previous hypothesis concerning carryover near the ground), a large reservoir of pollutants may be sequestered above it (Zhao and Hardesty, 1999). This reservoir may begin less than one hundred meters above the ground and end 1500 meters or more above the ground. In this discussion, the layer of air above the NBL is referred to as "aloft." Pollutants that carry over aloft may have a strong effect on surface ozone measurements the following day (Zhang and Rao, 1999).

At sunrise, the air aloft is usually isolated from the NBL due to a surface-based temperature inversion. As the sun rises, the Earth's surface warms and in turn warms the air near it. The warm air rises and mixes with air from aloft. This convective mixing erodes the temperature inversion, and pollutants aloft mix down to the surface, a process called fumigation. In this way, ozone and other pollutants that carry over aloft can interact with fresh emissions and may strongly affect today's ground-level ozone concentrations.

Photochemical conditions within pollutant reservoirs aloft

Reaction products of VOCs emitted the previous day are likely to comprise a large portion of the VOCs in pollutant reservoirs aloft. Many of these reaction products are VOC species that are ready to participate in ozone-forming processes as soon as solar radiation is supplied. In addition, virtually all the NO_X in reservoirs aloft is NO_2 and NO_X may be stored in other compounds, such as HONO and PAN. In reservoirs aloft, there is good reason to anticipate NO_x -limited photochemistry in the presence of very low NO_X concentrations. To understand the ozone WE effect, it may be important to know what happens when NO_X-limited reservoirs mix with VOC-limited fresh emissions the following day.

- **Hypothetical expectations and related observations**

If the carryover aloft hypothesis contributes substantially to the weekend effect, the expectations below are reasonable. With each expectation, related observations are given to help evaluate the plausibility of the hypothesis.

Expectation: Large reservoirs of ozone and ozone precursors aloft should be the routine rather than exceptional. The ozone weekend effect occurs routinely. If carryover plays a significant role, it should also be a common occurrence.

Observation: Meteorological data show that surface cooling begins in the late afternoon or early evening routinely. This surface cooling causes vertical mixing to break down, separating the cooler surface air from the warmer air above. As the surface air becomes disconnected from the air aloft, pollutants in the air aloft are certainly sequestered, at least temporarily. If winds aloft do not move these sequestered pollutants away and replace them with relatively clean air, a substantial reservoir of materials carries over to the following day. Direct measurements of pollution aloft are limited. Nevertheless, many field studies have found large amounts of pollutants aloft as photochemical processes begin at sunrise. Table 3-1 summarizes measurements aloft using ozonesondes (balloons) during the 1997 Southern California Ozone Study (SCOS97). Data for other pollutants are more difficult to collect, but the presence of large quantities of ozone may imply that some other pollutants are also plentiful aloft.

Table 3-1. Carryover of ozone from the previous day in a layer of polluted air above the ground surface. Pollutants within 1500 m of ground level are likely to contribute to pollutant measurements at the surface the next day.

Location	No. of Days	Ozone Concentration (ppb)								
		Surface			200 to 1000m**			200 to 1500m**		
		Avg	Min	Max	Avg	Min	Max	Avg	Min	Max
Anaheim	13	6	3	12	45	24	61	48	30	64
Central LA	11	7	3	22	44	25	62	48	32	65
CSU Northridge	13	10	3	56	51	35	71	52	39	72
Pomona	13	6	2	10	50	21	68	51	27	62
Riverside	13	10	2	29	47	23	67	47	28	64

* data from 8 a.m. ozonesondes during the 1997 Southern California Ozone Study
** elevation above ground level

Expectation: Pollutants aloft should begin to mix down to the surface some hours before the ozone maximum is recorded.

Observation: Special studies indicate that pollutants aloft begin to mix down to the surface before 10:00 a.m. on a routine basis.

Expectation: The photochemical system aloft should be NO_X-limited.

Observation: The data needed to fully substantiate this expectation are not available. Nevertheless, the limited data available indicate that ozone formation aloft may be strongly NO_X-limited (Anderson and Blumenthal, 1999; Sillman, 1999). Photochemistry tends to shift from VOC-limited to NO_X-limited over time; surface measurements demonstrate that this transition occurs as air parcels travel downwind horizontally, away from NO_X sources. The air aloft has also traveled "downwind", vertically rather than horizontally, and is likely to be NO_X-limited (Sillman, 1999). Carryover of ozone aloft may hasten the conversion of NO to NO_2 as warm air parcels rise from the surface into the air above. Because surface air quality data are strongly affected by fresh emissions continually emitted at the surface, these data do not accurately represent the ozone-forming system aloft, where most ozone is formed. The VOC data from samples collected aloft have rarely been analyzed using methods that would fully account for the reaction products of VOC photochemistry. Since these reaction products should comprise a large portion of the VOCs aloft, it is difficult to determine a characteristic VOC/NO_X ratio for pollutant reservoirs that carry over aloft. Preliminary analysis of VOC/NO_Y measurements collected aloft by aircraft during SCOS97 indicates variable ratios that are generally comparable to, and frequently higher than, VOC/NO_X ratios measured at surface monitoring sites. Because NO_Y concentrations are higher than NO_X concentrations (particularly downwind of the emission source), VOC/NO_X ratios aloft are typically higher than the corresponding ratio measurements at ground level. Unlike surface-based measurements, the measurements aloft indicate that the morning ratios are generally higher than the afternoon ratios. This observation is consistent with the morning ratios reflecting carryover and atmospheric processes removing NO_X faster than VOCs while the afternoon ratios reflect the influence of fresh emissions from the surface being mixed up into the air compartment aloft during the period of day with deeper atmospheric mixing.

Expectation: The mix of VOCs during the hours leading up to the ozone maximum should be “older” on weekends compared to weekdays.

Observation: As an air mass "ages", directly emitted VOCs are converted to oxygenated reaction products. Analyses of samples collected at the surface on weekdays and weekends suggest that the weekend samples have a larger fraction of species associated with older emissions. Routine analyses, however, are often conducted by methods that make the results unsuitable for use in assessing this issue.

Expectation: As pollutants from reservoirs aloft mix with fresh emissions they should rapidly convert NO to NO_2. Because less NO is emitted on weekends, the NO_2 to NO ratio in the ambient air should be higher on weekends than on weekdays as long as the fresh emissions are mixing with materials from reservoirs aloft.

Observation: In the SoCAB, hourly day-of-week profiles for the NO_2 to NO ratio at ground level show that the ratio is higher on weekends throughout the daylight hours at almost all locations. Only trace amounts of NO occur aloft (Anderson and Blumenthal, 1999) so almost all NO_X aloft is in more oxidized forms of NO. Measured amounts of “NO_X”, however, often include other compounds, such as PAN, that readily contribute to ozone-forming reactions. The mixing of aged pollutants aloft, especially ozone, with fresh NO emissions destroys the ozone but converts the NO to NO_2.

- **Limitations**

The ability to critically assess the carryover aloft hypothesis is severely restricted by the lack of data that represent a broad spectrum of situations. Intensive sampling efforts during field studies are usually limited to days with the potential to form high concentrations of ozone. Little data on the air aloft has been collected on other types of days. Even during intensive sampling periods, vital types of data have not been collected. In some cases, the methods needed to collect the necessary data do not exist or are excessively expensive. In other cases, those conducting the study were not aware of the need for certain types of data, so they did not attempt to gather it.

Hypothesis #5: Increased weekend emissions

- **Synopsis**

According to the increased weekend emissions hypothesis, higher weekend ozone levels in at least some locations are caused by increased emissions and/or increased reactivity of VOC emissions from activities that occur more often on weekends than on weekdays.

The increased weekend emissions hypothesis further proposes that the total emissions of VOCs and/or NO_X in some areas of the SoCAB increase on weekends rather than decrease; increased emissions then lead to local increases in ozone on weekends. Suburban residential regions and areas with high levels of recreational activity are prime candidates for these phenomena.

- **Theory**

According to the increased weekend emissions hypothesis, higher weekend ozone levels are caused by increased emissions or by greater reactivity of emissions on weekends. That is, some activities take place predominantly on weekends and emissions from these activities <u>more than offset</u> any reductions in activities that decrease on weekends.

If this hypothesis is relevant to more than a few locations, then some significant and ubiquitous sources of ozone precursors must increase their activities substantially on weekends. At least two emission categories – diurnal evaporative emissions from motor vehicles and emissions from home maintenance activities, such as painting and lawn and garden activity – may increase on weekends and qualify as significant and ubiquitous.

Weekend increases in emissions are likely to emphasize VOCs rather than NO_X. Activities such as lawn and garden care and recreational boating, for example, are relatively rich in VOC emissions and can produce large amounts of emissions for several reasons (relatively loose standards, poor maintenance, age, etc.).

Although this hypothesis may not apply generally, ozone at selected sites might reflect local increases in precursors due to weekend increases in some activities.

- **Hypothetical expectations and related observations**

If the Increased Weekend Emissions hypothesis contributes substantially to the weekend effect, the expectations below are reasonable. With each expectation, related observations are given to help evaluate the plausibility of the hypothesis.

Expectation: Comparisons of day-specific emission inventories should identify increased emissions or increased reactivity of emissions on weekends.

Observation: Although some types of activities increase significantly on weekends, these activities are unlikely to offset large reductions in major source categories in most areas.

Expectation: Ambient concentrations of VOCs and/or NO_X should be greater on weekends compared to weekdays at more than a few sites.

Observation: On weekends, ambient NOx concentrations seem to be lower throughout the daylight hours compared to weekdays. As a surrogate for VOCs, CO concentrations on Saturdays may exceed the weekday concentrations at some locations. On Sundays, however, CO levels at most sites seem to be lower than on weekdays throughout the daylight hours. Sunday, however, is the day with the highest ozone, so increased weekend emissions does not seem to be a plausible explanation.

- **Limitations**

Complete inventories of emissions on weekends are still being developed. When they are ready, these inventories might guide the design of field studies that might find areas with significantly increased emissions on weekends.

The limited scope of VOC sampling in many areas leaves some possibility (although limited) for the future discovery of areas in which ambient VOC concentrations are higher on weekends than on weekdays.

Hypothesis #6: Aerosols and UV radiation

- **Synopsis**

This hypothesis presumes that the amount of soot (elemental carbon) and other particles in the atmosphere is greater on weekdays than on weekends. Furthermore, this difference strongly affects ozone formation because soot absorbs, and other particles can scatter or absorb, ultraviolet sunlight that would otherwise participate in ozone-forming photochemical processes.

Large numbers of vehicles, including heavy-duty diesel trucks, emit soot and other particles on weekdays. On weekends, however, traffic is greatly reduced during the morning and less soot and particles are emitted. The lower soot concentrations on weekends absorb less ultraviolet sunlight, thereby permitting more photochemical activity on the weekend, which in turn increases ozone formation on weekends. Thus, reduced soot particles contribute to higher ozone concentrations on weekends compared to weekdays.

- **Theory**

Actinic flux

Ultraviolet light of specific wavelengths is needed to initiate the processes that form ozone in the troposphere. The total amount of photochemically active light that passes through a part of the atmosphere is called the “actinic flux.” The actinic flux includes light arriving from all directions.

Particles and actinic flux

Depending on several factors, particles can increase or decrease the actinic flux at a location. At some times, the presence of particles in the air can increase actinic flux above normal levels by scattering ultraviolet light. When light scatters, it usually travels a longer path in the atmosphere before being absorbed, passing through the atmosphere, or being reflected back out to space. Therefore, the total number of ultraviolet photons in a particular volume of air may increase.

Soot particles and some organic molecules (Malm et al., 1996), on the other hand, decrease actinic flux by absorbing ultraviolet light. When soot absorbs ultraviolet light, the energy is typically re-radiated as heat, which does not initiate ozone-forming chemical reactions. In addition to light absorption and scattering effects, particles also provide surfaces upon which chemical reactions can occur. Ozone tends to have a negative association with aerosols (Berkowitz et al., 2001). In addition, it is likely that NO_2 can react with aerosols and affect ozone production (Arens et al., 2002). Thus, this hypothesis and associated side effects are complex.

- **Hypothetical expectations and related observations**

If the Aerosols and UV radiation hypothesis contributes substantially to the weekend effect, the expectations below are reasonable. With each expectation, related observations are given to help evaluate the plausibility of the hypothesis.

Expectation: Comparisons of vehicle activity on weekdays and weekends should show significant decreases on weekends.

Observation: The day-of-week activity patterns for heavy-duty trucks (HDT) shown in Figure 3-5 indicate vastly reduced HDT activity on weekends. Since diesel trucks are a large source of light-absorbing particles, more solar radiation may be available on weekends to drive the photochemical system. However, some limited evaluations of the potential magnitude of this effect suggest it is not a large contributor to the ozone weekend effect.

Expectation: Ambient levels of soot particles should be significantly smaller on weekends compared to weekdays.

Observation: The available data do not provide sufficient information about ambient levels of soot particles to assess the significance of this hypothesis. Methods of identifying diesel particulate matter are still being developed. Concentrations of particulate matter generally tend to decline on weekends but less is known about the variations in the number, size, and composition of the particles.

Expectation: Measurements of actinic flux at the surface or within the mixing layer should be greater on weekends compared to weekdays.

Observation: Measurements of total incident energy from solar radiation do not indicate a large difference between weekends and weekdays.

- **Limitations**

Data on actinic flux are only rarely available. Methods of identifying diesel particulate matter in the air are still being developed.

Hypothesis #7: Surface O_3 quenching

- **Synopsis**

The other six hypotheses focus on how more ozone might be created on weekends than on weekdays. The surface O_3 quenching hypothesis, however, asserts that less ozone is destroyed on weekends than on weekdays.

Less destruction of ozone on weekends is attributed to reduced emissions of NO_X on weekends compared to weekdays. The mechanism that destroys ozone is $NO + O_3 \rightarrow NO_2 + O_2$ (equation 7 in Chapter 2), a reaction sometimes referred to as ozone “titration”, "scavenging", or "quenching".

Emissions of NO_x are predominantly NO and are mostly released near the ground. Quenching of O_3 by NO reduces the amount of O_3 measured in air near NO sources (e.g., ground level monitors). The greater NO emissions on weekdays destroy more O_3 compared to the lower NO emissions on weekends. Ozone levels are higher on weekends because less O_3 is destroyed and more survives to be measured at ground level on weekends compared to weekdays.

- **Theory**

The nitric oxide (NO) in NO_x emissions destroys or "quenches" ozone via a fast reaction in which O_3 and NO change to O_2 and NO_2 ($NO + O_3 \rightarrow NO_2 + O_2$).

Emissions of NO in urbanized areas are abundant on weekdays but relatively scarce on weekends, particularly on Sunday mornings. Fresh NO emissions at ground level quickly quench ozone molecules and reduce the ozone concentrations measured by surface monitors. This quenching phenomenon is much greater on weekdays than on weekends, and it may be a major cause of the ozone weekend effect.

- **Hypothetical expectations and related observations**

If the surface O_3 quenching hypothesis contributes substantially to the weekend effect, the expectations below are reasonable. With each expectation, related observations are given to help evaluate the plausibility of the hypothesis.

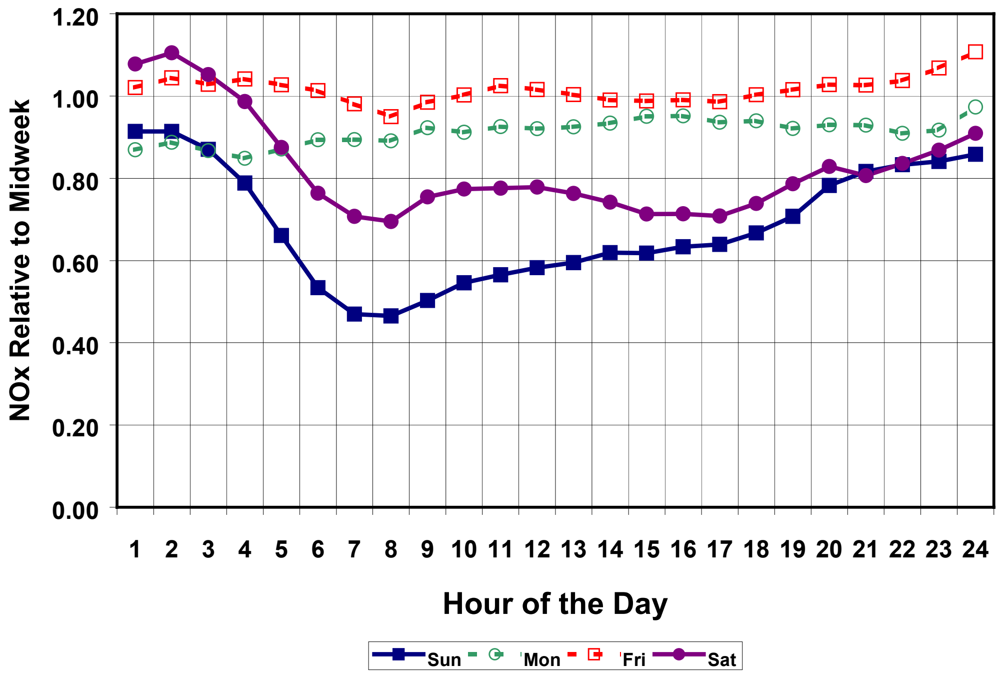
Expectation: Ambient levels of NO_X will be substantially lower on weekends than on weekdays. As a result, the ratio NO_X on weekends to NO_X on weekdays should be lower for corresponding daylight hours, particularly during the hours leading to when ozone is likely to reach its maximum levels each day.

Observation: Measurements of ambient NO_X in the SoCAB indicate that weekend NO_X emissions during daylight hours are almost 40% lower than weekday NO_X emissions (Figure 3-7). Furthermore, the fraction of ambient NO_X that is NO is smaller on weekends than on weekdays, so the amount of NO available for quenching ozone near the ground is even lower than indicated in Figure 3-7. Compared to weekdays, the potential for ozone quenching near the surface is approximately 20-30% lower on Saturdays and 40-50% lower on Sundays.

Expectation: If VOC emissions are reduced faster than NO_x emissions, ozone levels should decrease on all days, but the magnitude of the ozone WE effect should increase. VOC reductions could cause less ozone to be produced on all days of the week. A slower reduction in NO emissions would cause NO to increase relative to the lower levels of ozone. The relatively greater NO emissions would quench a larger fraction of ozone near the surface of the ground. The fraction of ozone quenched by high NO emissions on weekdays would grow in relation to the fraction of ozone quenched by lower NO emissions on weekends, so the apparent WE effect would increase.

Observation: Over the last twenty years, VOC emission reductions have been substantially greater than NO_x emission reductions throughout California. In the South Coast Air Basin, the rate of VOC reductions has been about 50% greater than the rate of NO_x reductions. Simultaneously, ozone levels decreased in the SoCAB on all days of the week. However, the ozone WE effect increased as ozone declined on weekdays faster than it declined on weekends. Greater ozone quenching on weekdays than on weekends may contribute to these observations.

Figure 3-7. Hourly NO_X values by day-of-week expressed as a percent of midweek (Tue-Thu) value; composite of 11 sub-regions of the South Coast Air Basin.



Expectation: Total oxidant is the sum of ozone and NO_2. As NO emissions quench ozone, they become NO_2. Therefore, the WE effect for total oxidant should be smaller than the WE effect for ozone.

Observation: Based on ambient air quality data for the SoCAB from May through October in 1998 through 2000, the largest WE effect for total oxidant was 9% and the basinwide average was 5%. These are drastically smaller than the values for the ozone WE effect, for which the largest was 43% and the average was 20%.

Expectation: If areas grow in population and in activity of ground-level NO_x sources, the ozone WE effect in those areas should increase.

Observation: Over the last twenty years, urbanization in the SoCAB as pushed further and further east. Population and VMT growth have been dramatic in inland areas. During this period, the magnitude of the ozone WE effect in these areas has also increased.

Expectation: Ozone concentrations should increase earlier on weekends than on weekdays. Because ozone aloft mixes downward to the surface as the mixing height deepens, the large amount of NO emissions on weekdays can quench the ozone that mixes downward. On weekends, however, substantially less NO is emitted to quench the ozone from aloft.

Observation: In areas where the ozone weekend effect occurs, ozone levels do increase earlier on weekends than on weekdays, even before substantial photochemical activity can begin.

Expectation: If surface ozone quenching is a significant cause of the ozone weekend effect, the difference between ozone aloft and ozone at the surface should be greater on weekdays than on weekends. These differences should also be present at the time of the day when surface ozone concentrations are highest.

Observation: Data from balloon-born instruments that measure ozone show that the difference between ozone aloft (100 meters above the surface) and ozone at the surface is typically greater on weekdays than on weekends. These results were found for balloons launched at 2:00 p.m., near the time of the day that surface ozone concentrations are highest.

- **Limitations**

Although the surface O_3 quenching hypothesis appears to play a major role in determining the ozone WE effect, isolating and quantifying its impact on peak ozone concentrations is a difficult task. All of the physical and chemical processes present affect ambient ozone levels and make it extremely difficult to isolate the effects. Process-oriented applications of improved photochemical models may be needed for this purpose.

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